

A New Conjugated Addition of Trialkyl Phosphites and Alkylidenephosphoranes to 3- ω -Azideoacetyl Coumarin Synthesis of Some 1,2,3,4-Triazaphospholes, Triazoles, and Azido-Coumarin Derivatives

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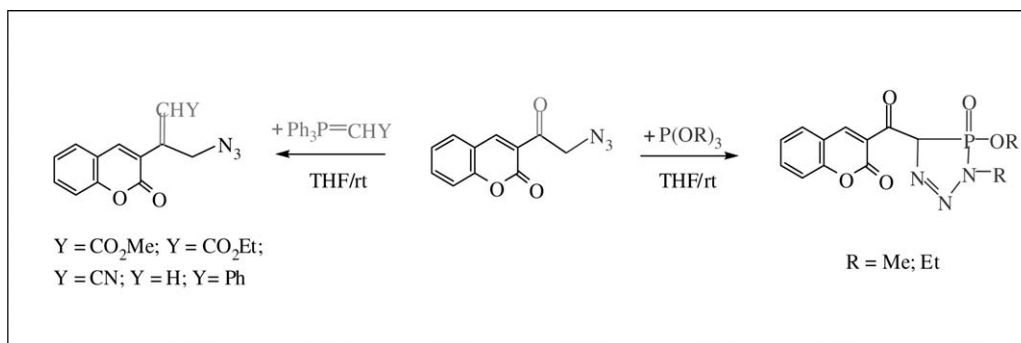
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A new and efficient conjugate addition of trimethyl and triethyl phosphites to 3- ω -azidoacetylcoumarin (**1**) has been studied. The reaction proceeded smoothly at r.t. furnishing 1,2,3,4-triazaphosphole coumarin derivatives **4a,b** in ~75% yields. Linear substituted triazoles **10a,b** were also obtained from the reactions of **1** with α -keto ylides, acetyl- and benzoylmethylene triphenylphosphoranes. Contrary to these results, Wittig reaction was occurred when **1** was allowed to react with α -alkoxycarbonylmethylene- and cyanomethylenetriphenylphosphoranes **7c-e** as well as with methylenetriphenylphosphoranes **8a,b** resulting in the formation of the corresponding olefins either as an intermediate **14b** or as final products **11a-c**.

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INTRODUCTION

A considerable number of naturally occurring coumarins such as Muttalongin, Usthol, and 2,3-Auraptin were found to have strong antimicrobial and anticancer activities [1]. Also, coumarin dyes recently have found great interests because of their high potential in dye laser to achieve tunable blue-green light and are also used in enzyme determination; photobiological energy transfer processes fluorescent probe technique; and fluorescence whiteners in detergent products [2].

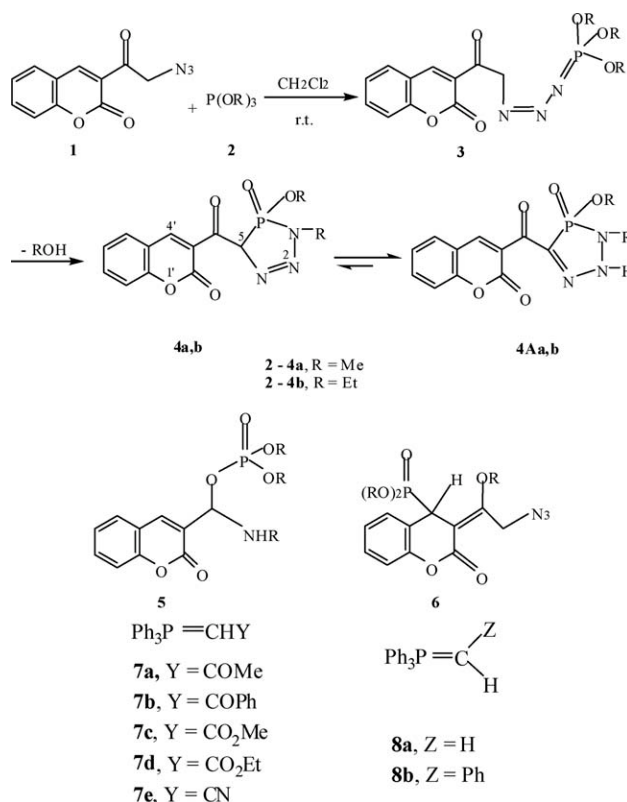
In continuation with our research program directed toward the utility of trivalent and pentavalent phosphorus reagents in synthesis of pharmaceuticals [3–12], we extend our precedent work on coumarins and relevant phosphor derivatives [13,14] to elaborate more novel coumarin derivatives of expecting pharmacological potenc. The methodology involved application of trialkyl phosphites and alkylidenephosphoranes to 3-azidoacetylcoumarin (**1**).

RESULTS AND DISCUSSION

The azide **1** reacted smoothly with trimethyl- **2a** and triethyl phosphite **2b** in absolute methylene chloride at room temperature and yielded, in each case, the tautomeric structure **4a,b** $\rightleftharpoons$ **4Aa,b** in $\approx$ 75% yield. Compound **4** can be viewed as derived from ring closure of the phosphazide **3**, initially formed [15,16] with concomitant extrusion of the appropriate alcohol moiety. Further rearrangement through alkyl group shift led to the triazaphosphole products **4a,b** (Scheme 1).

Compounds **4a,b** showed ³¹P-NMR chemical shifts around δ 11.4 ppm confirming the presence of N–P–C linkage in a phosphole moiety and readily eliminate any formation of phosphates for which a signal at δ p = $\pm$ 2–4 ppm would be expected. The IR spectrum of **4a** revealed the presence of absorption bands at 1722 (C=O, lactone), 1633 (C=O, acetyl), 1265 (P=O, free), and at 1055 (P–O–CH₃) cm^{–1}. Moreover, the strong azide frequency present in the IR spectrum of **1** at 2093 cm^{–1} was absent in the IR spectra of **4**. In the

Scheme 1



1H -NMR [17] spectrum of **4a** ($CDCl_3$), the 4'-H of coumarin was observed as a singlet at δ 8.68 ppm. A doublet (3H, $^3J_{P-H} = 8.8$ Hz) was observed at δ 3.66 due to OCH_3 protons attached to the phosphorus atom. A doublet (3H, $^3J_{P-H} = 8.3$ Hz) was observed at δ 3.27 assigned to the CH_3 protons linked to the 3-N in the triazaphosphole ring. The singlet due to the methylene protons linked to the azide group present in the pmr spectrum of **1** at δ 4.73 ppm was absent in the spectrum of **4a**. Instead, a doublet (1H, $^2J_{P-H} = 23.4$ Hz) was displayed at δ 5.16 due to 5-H (**4a**). Remarkably, the structure **4Aa** (Scheme 1) cannot be overlooked since a weak broad signal was displayed at 3339 cm^{-1} in the IR spectrum assigned to an NH group; this signal appeared at δ 11.42 (br) in its pmr spectrum. It is noteworthy that the position of N-(H) hydrogen atom in triazoles such as structure **4** has been the subject of contradictory discussion [18]. Furthermore, the ^{31}P -NMR chemical shifts; the presence of 5-H as a doublet of high coupling constant and 4'-H coumarin singlet, and the lack of a singlet due to the methylene group in the pmr spectrum, as well as the absence of the azido group in its ir spectrum, confirm the assigned structures **4** $\rightleftharpoons$ **4A** and rule out other alternative structures like **5** and **6**.

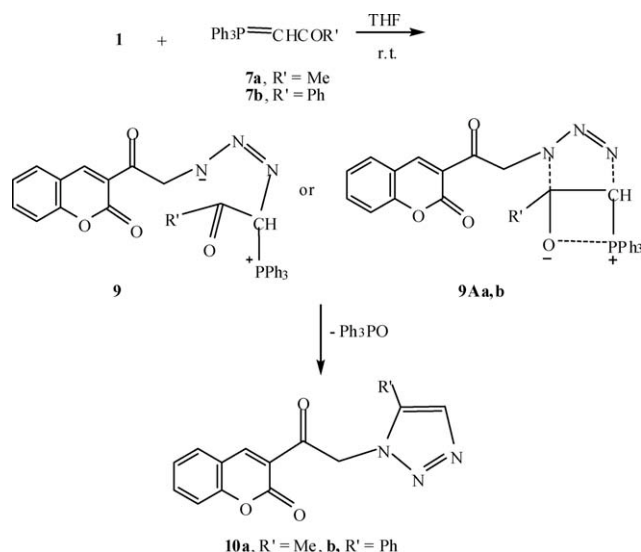
Next, the study has been extended to investigate the interaction of the azide compound **1** with three types of

stabilized Wittig reagents: i- α -ketomethylene-**7a,b**, ii- alkoxycarbonyl-methylene-**7c,d**, iii- cyanomethylene-triphenylphosphorane **7e**; and two active ylides: i- methylenide- (**8a**) and benzyldenetriphenylphosphorane (**8b**).

When the azide **1** was treated with acetylmethylene-**7a** or benzoylmethylenetriphenyl-phosphorane (**7b**) in tetrahydrofuran (THF) at room temperature for 24 h, 1,2,3-triazoloactyl-coumarins **10a,b** were formed in $\sim 74\%$ yield. Triphenylphosphine oxide (TPPO) was also isolated from the reaction medium. The triazole structure **10** was deduced from analytical and spectroscopic data. In the IR spectrum of **10a**, the lactone carbonyl was observed at 1721 cm^{-1} and that of the 3-acetyl carbonyl group observed at 1685 cm^{-1} . In its 1H -NMR, the protons of methylene group were observed downfield as a singlet at δ 5.37 ppm.

As depicted in Scheme 2, a 1,3-dipolar addition of the azide **1** on the $P=C$ bond of the ylide **7a,b** followed by elimination of TPPO from the cyclic intermediate **9** afforded *N*-1-substituted-5-methyl (or 5-phenyl)-1,2,3-triazoles **10a,b** [19–23]. The formation of the triazoles from treating **1** with **7a,b** adequately demonstrates the regiochemistry [23] of the reaction that leads to the exclusive formation of 1,5- instead of 1,4-disubstituted triazoles. Furthermore, the formation of **10** through either a two step addition, *via* the intermediate **9**, or a

Scheme 2

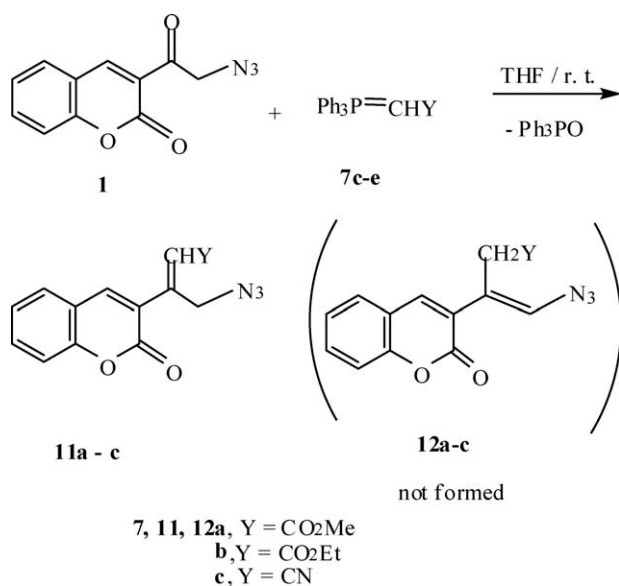


concerted cycloaddition, *via* the transition state **9A**, is consistent with the observed result.

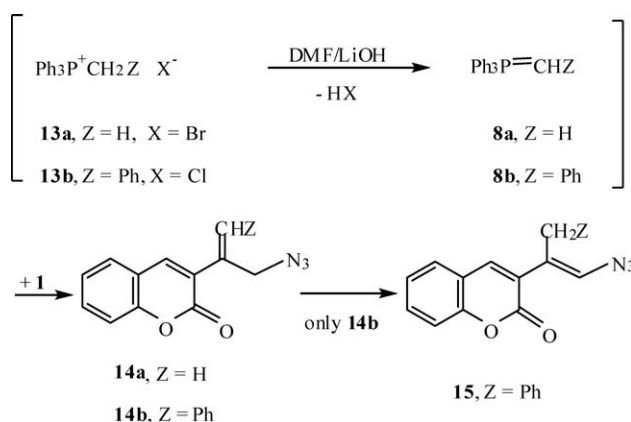
In the contrary to the behavior of trialkyl phosphites and α -keto ylides, the reactions of **1** with α -alkoxy carbonyl- and α -cyanomethylenetriphenylphosphoranes (**7c-e**), performed under similar conditions, followed the Wittig reaction, gave coumarin-azido-derivatives **11a-c** in $\approx 70\%$ yields. Compounds **11a-c** were obtained as *Z*-isomers predominantly based of spectroscopic data and due to steric demand of the transition states to form the oxaphosphetane **9A** (Scheme 3) [24–27].

The spectroscopic data of compounds **11a-c** are in agreement with the assigned structure. In the EI mass

Scheme 3



Scheme 4



spectra, they showed the molecular ion peaks (M^+ %) that displayed the expected fragmentations of the corresponding spectrum. The most characteristic signals in their ^1H -NMR spectra are those of the methylene (CH_2N_3) and the methinic ($=\text{CHY}$) protons, which appeared as a doublet and a triplet each with $^4J_{\text{H-H}} = 1.6$ Hz at δ 4.44–4.23 and 6.08–6.28, respectively. The presence of ($=\text{CHY}$) and (CH_2N_3) moieties were also attested by signals at δ 112–98, and 55–52 ppm in ^{13}C -NMR spectra. These recorded data for the methine ($=\text{CH}$) and the methylene protons could readily eliminate structure like **12**, which would predict a doublet at ~ 3.5 and a triplet at ~ 7.3 ppm.

Further extension of this study to other ylides, application of methylidene- (**8a**) and benzylidene-triphenylphosphorane (**8b**) to **1** was investigated. When dimethylformamide (DMF) solution of an equivalent amounts of **1** and **8a**, prepared in situ from its bromide salt **13a**, in the presence of aqueous LiOH was stirred at rt for 12 h, the reaction afforded the Wittig product **14a** (80%), on the basis of comparable spectroscopic arguments (Scheme 4).

On the other hand, the reaction of **1** with slight excess (10%) of **8b** (prepared in situ from its chloride salts, **13b**) under the same conditions gave the benzylvinyl derivative **15** (84%), which is an isomer of the Wittig product **14b** (Scheme 4).

In summary, the condensation of trialkyl phosphites and alkylidenephosphoranes (resonance-stabilized- and active ylides) with 3-azidoacetyl coumarin resulted in an interesting spectrum of the reactivity. Furtherward, the structural products (**4a,b**, **10a,b**, **11a-c**, **14a**, and **15**) obtained from the four studied reactions, however, indicated two positions in **1** that are susceptible to nucleophilic attack by the phosphorus reagents. The first position relates to an attack at the azide group; this addition was observed by trialkyl phosphites and α -keto

ylides, which afforded, via 1:3-dipolar intermediates, 1,2,3,4-triazaphosphole and triazolylacetyl-coumarin derivatives, respectively. The second site of attack is concerned with the attack of the ylides **7c–e** and **8a,b** at the acetyl carbonyl carbon group, which led to the respective olefins.

Finally, the synthesized heterocyclic phosphole system **4a,b** that included a phosphorus linked to a nitrogen atom are of great interest because this system is common to a diverse array of important biological molecules.

EXPERIMENTAL

General: Melting points were determined with open capillary tube on an Electrothermal (variable heater) melting point apparatus and were uncorrected. IR spectra were recorded on a Perkin–Elmer spectrophotometer model 297 using KBr disc. NMR spectra were measured with a JEOL E.C.A-500 MHz (^{13}C : 125.7 MHz, ^1H : 500 MHz, ^{31}P : 202.4 MHz) spectrometer. ^{31}P -NMR spectra were recorded with H_3PO_4 (85%) as external reference. ^1H - and ^{13}C -NMR spectra were recorded with trimethylsilane as internal standard in CDCl_3 or $\text{DMSO}-d_6$. Chemical shifts (δ) are given in ppm. The mass spectra were performed at 70 eV on an MS-50 Kratos (A.E.I.) spectrometer provided with a data system. The appropriate precautions in handling moisture-sensitive compounds were observed. Materials and reagents were purchased from Aldrich Company. The substrate, 3-azidoacetylcoumarin **1** was prepared according to the reported method [15].

Reaction of 3-azidoacetylcoumarin (1) with trialkyl phosphites 2a,b. Preparation of compounds 4a and 4b. To a solution of 0.8 g (3.5 mmol) of the azide **1** in 25 mL of absolute CH_2Cl_2 at 0°C , 3.5 mmol of freshly distilled trimethyl- **2a** or triethyl phosphite **2b** were added dropwise with stirring. After the addition was complete, the reaction mixture was stirred at room temperature for 6 h, and the solvent was evaporated to dryness. The residue was washed several times with light petroleum ($40\text{--}60^\circ\text{C}$) and crystallized from the proper solvent to give **4a** or **4b**, respectively.

3-[(4-Methoxy-3-methyl-4-oxido-4,5-dihydro-3H-1,2,3,4-triazaphosphol-5-yl)-carbonyl]-2H-chromen-2-one (4a). This was obtained as straw yellow needles, 863 mg (77%); mp $170\text{--}172^\circ\text{C}$ (cyclohexane); IR: ν_{max} NH 3339 (**4Aa**), $2\text{C}=\text{O}$ 1722, 1633, $\text{P}=\text{O}$, free 1265, 1055 ($\text{P}-\text{O}-\text{C}$) cm^{-1} ; ^1H -NMR ($\text{DMSO}-d_6$): δ 3.27 (d, $^3J_{\text{P-H}} = 8.3$ Hz, 3H, NCH_3), 3.66 (d, $^3J_{\text{P-H}} = 8.8$ Hz, 3H, POCH_3), 5.16 (d, $^2J_{\text{P-H}} = 23.4$ Hz, 1H, 5'-H, **4a**), 7.32 (t, $J_{\text{H-H}} = 7.4$ Hz, 2H, 6'-H and 7'-H), 7.52 (d, $J_{\text{H-H}} = 7.8$ Hz, 2H, 5'-H and 8'-H), 8.68 (s, 1H, 4'-H), 11.42 ppm (br, 1H, NH, **4Aa**); ^{13}C -NMR ($\text{DMSO}-d_6$): δ 177.4 (d, $^2J_{\text{P-C}} = 5.8$ Hz, $\text{C}=\text{O}$), 158.8 ($\text{C}=\text{O}$, lactone), 153.3 (9'-C), 147.7 (4'-C), 134.3, 131.5, 126.4, 118.7, 116.2 (7'-C, 8'-C, 5'-C, 6'-C, 10'-C), 133 (d, $^1J_{\text{P-C}} = 139$ Hz, 5-C-P, **4Aa**), 120.2 (d, $^3J_{\text{P-C}} = 4.4$ Hz, 3'-C), 65.3 (d, $^1J_{\text{P-C}} = 141$ Hz, 5-C-P), 55.1 (d, $^2J_{\text{P-C}} = 7.5$ Hz, POCH_3), 28.8 ppm (d, $^2J_{\text{P-C}} = 7$ Hz, N-CH_3); ^{31}P -NMR ($\text{DMSO}-d_6$): δ 11.4 ppm; ms: m/z (EI): 323 [$\text{M}^+ + 2$, 80 %], 321 [M^+ , 100%], 306 (16), 291 (31), 252 (83), 228 (33), 227 (24), 213 (19), 188 (18), 173(43), 170 (10), 77 (18). Anal. Calcd. for

$\text{C}_{13}\text{H}_{12}\text{N}_3\text{O}_5\text{P}$ (321.2): C, 48.61; H, 3.77; N, 13.08; P, 9.64. Found: C, 48.68; H, 3.82; N, 13.15; P, 9.59.

3-[(4-Ethoxy-3-ethyl-4-oxido-4,5-dihydro-3H-1,2,3,4-triazaphosphol-5-yl)-carbonyl]-2H-chromen-2-one (4b) This was obtained as yellow needles, 0.9 g (74%); mp $132\text{--}134^\circ\text{C}$ (cyclohexane); IR: ν_{max} NH 3384 (**4Ab**), $2\text{C}=\text{O}$ 1722, 1638, $\text{P}=\text{O}$, free 1258, 1088 ($\text{P}-\text{O}-\text{C}$) cm^{-1} ; ^1H -NMR ($\text{DMSO}-d_6$): δ 1.03–1.31 (2dt (m), 6H, NC-CH_3 and POC-CH_3), 3.99 (dq, $^3J_{\text{H-H}} = 6.4$, $^3J_{\text{P-H}} = 4.8$ Hz, 2H, NCH_2), 4.09 (dq, $^3J_{\text{H-H}} = 6.4$, $^3J_{\text{P-H}} = 4.8$ Hz, 2H, POCH_2), 5.09 (d, $^2J_{\text{P-H}} = 23.4$ Hz, 1H, 5'-H, **4b**), 7.35 (t, $J_{\text{H-H}} = 7.4$ Hz, 2H, 6'-H and 7'-H), 7.57 (d, $J_{\text{H-H}} = 7.8$ Hz, 2H, 5'-H and 8'-H), 8.64 (s, 1H, 4'-H), 11.14 ppm (br, 1H, NH, **4Ab**); ^{13}C -NMR ($\text{DMSO}-d_6$): δ 177.6 (d, $^2J_{\text{P-C}} = 5.8$ Hz, $\text{C}=\text{O}$), 158.8 ($\text{C}=\text{O}$, lactone), 154.7 (9'-C), 147.8 (4'-C), 134.7, 130.6, 126.4, 118.3, 117.6 (7'-C, 8'-C, 5'-C, 6'-C, 10'-C), 136 (d, $^1J_{\text{P-C}} = 139$ Hz, 5-C-P, **4Ab**), 120.4 (d, $^3J_{\text{P-C}} = 4.4$ Hz, 3'-C), 67.4 (d, $^1J_{\text{P-C}} = 144$ Hz, 5-C-P), 62.5 (d, $^2J_{\text{P-C}} = 7.5$ Hz, POCH_2), 44.1 (d, $^2J_{\text{P-C}} = 7$ Hz, N-CH_2), 19.6 (d, $^3J_{\text{P-C}} = 5.8$ Hz, POC-CH_3), 14.4 ppm (d, $^3J_{\text{P-C}} = 5.8$ Hz, N-CH_3); ^{31}P -NMR ($\text{DMSO}-d_6$): δ 10.8 ppm; ms: m/z (EI): 351 [$\text{m}^+ + 2$, 26%], 349 (74) [m^+], 320 (17), 291 (37), 263(100), 252 (71), 227 (83), 213 (20), 188 (13), 173(53), 170 (15), 77 (18); Anal. Calcd. for $\text{C}_{15}\text{H}_{16}\text{N}_3\text{O}_5\text{P}$ (349.3): C, 51.58; H, 4.62; N, 12.03; P, 8.87. Found: C, 51.65; H, 4.57; N, 12.11; P, 8.91.

Reaction of 1 with ketomethylenetriphenylphosphorane-s7a,b. Preparation of compounds 10a and 10b. A mixture of azide **1** (0.8 g, 3.5 mmol) and acetyl- **7a** (1.3 g, 3.5 mmol) or benzoylmethylenetriphenylphosphorane (**7b**) (1.1 g, 3.5 mmol) in 30 mL of dry tetrahydrofuran (THF) was stirred at rt for 24 h. After removing the solvent, the residue was chromatographed on silica gel to afford the triazoles **10a** or **10b**. Triphenylphosphine oxide (Ph_3PO) was also isolated.

3-[(5-Methyl-1H-1,2,3-triazol-1-yl)acetyl]-2H-chromen-2-one (10a). This was obtained as yellow crystals, 705 mg (75%); mp $158\text{--}160^\circ\text{C}$ (MeCN); IR: ν_{max} $2\text{C}=\text{O}$ 1721, 1685 cm^{-1} ; ^1H -NMR ($\text{DMSO}-d_6$): δ 2.38 (d, $J_{\text{H-H}} = 2.3$ Hz, 3H, 5-C- CH_3), 5.37 (s, 2H, $\text{C}(\text{O})\text{CH}_2$), 7.34 (d, $J_{\text{H-H}} = 7.4$ Hz, 2H, 6'-H and 7'-H), 7.55 (d, $J_{\text{H-H}} = 7.8$ Hz, 2H, 5'-H and 8'-H), 7.58 (q, $J_{\text{H-H}} = 2.3$ Hz, 1H, 4'-H), 8.65 ppm (s, 1H, 4'-H); ^{13}C -NMR ($\text{DMSO}-d_6$): δ 187.4 ($\text{C}=\text{O}$, acetyl), 161.2 (2'- $\text{C}=\text{O}$), 154.7 (9'-C), 148.7 (4'-C), 142.8 (5-C), 138.3 (4-C), 134.3, 131.5, 126.4, 118.7, 114.2 (7'-C, 8'-C, 5'-C, 6'-C, 10'-C), 121.6 (3'-C), 53.8 (CH_2 , acetyl), 13.3 ppm (5-C- CH_3); ms: m/z (EI): 270 (27) [$\text{M}^+ + 1$], 269 (22) [M^+], 254 (26), 237 (100), 188 (63), 172 (53), 170 (15), 145 (18), 77 (16). Anal. Calcd. for $\text{C}_{14}\text{H}_{11}\text{N}_3\text{O}_3$ (269.3): C, 62.45; H, 4.12; N, 15.61. Found: C, 62.52; H, 4.06; N, 15.64.

3-[(5-Phenyl-1H-1,2,3-triazol-1-yl)acetyl]-2H-chromen-2-one (10b). This was obtained as yellow crystals, 855 mg (74%); mp $186\text{--}188^\circ\text{C}$ (MeCN); IR: ν_{max} $2\text{C}=\text{O}$ 1720, 1680 cm^{-1} ; ^1H -NMR ($\text{DMSO}-d_6$): δ 5.27 (s, 2H, $\text{C}(\text{O})\text{CH}_2$), 7.24–7.37 (m, 3H, H-Ph and H-Ar), 7.46–7.66 (m, 6H, H-Ph and H-Ar), 8.02 (s, 1H, 4'-H), 8.53 ppm (s, 1H, 4'-H); ^{13}C -NMR ($\text{DMSO}-d_6$): δ 186.7, 160.4 ($2\text{C}=\text{O}$), 154.7 (9'-C), 148.7 (4'-C), 142.8 (5-C), 134.3 (4-C), 131.5, 130.5, 129.2, 126.4, 125.7, 123.6, 123.1, 122.6, 118.7, 114.2 (C-Ph and C-Ar), 121.6 (3'-C), 53.8 (CH_2 , acetyl); ms: m/z (EI): 333 (36) [$\text{M}^+ + 2$], 331(100) [M^+], 303 (92), 289 (78), 288 (51), (26), 237 (100), 188 (63), 172 (53), 170 (15), 145 (18), 77 (14). Anal. Calcd. for $\text{C}_{19}\text{H}_{13}\text{N}_3\text{O}_3$ (331.3): C, 68.88; H, 3.95; N, 12.68. Found: C, 68.85; H, 4.01; N, 12.62.

Reaction of 1 with alkylidenetriphenylphosphoranes 7c–e. **Preparation of compounds 11a, 11b, and 11c.** A mixture of the azide **1** (0.8 g, 3.5 mmol) and 3.5 mmol of methoxycarbonyl- (**7c**), ethoxycarbonyl- (**7d**), or cyanomethylenetriphenylphosphorane (**7e**) in 30 mL THF was stirred at r.t. for 24 h. After removing the solvent, the residue was chromatographed on silica gel to afford **11a**, **11b**, or **11c**, respectively. Ph_3PO was also isolated.

Methyl (2Z)-4-azido-3-(2-oxo-2H-chromen-3-yl)but-2-enoate (11a). This was obtained as yellow crystals, 657 mg (66%); mp 165–167°C (CHCl_3); IR: ν_{max} C–N₃ 2112, C=O (lactone) 1721, C=O (ester) 1713, C=C (exocyclic) 1611 cm^{-1} ; $^1\text{H-NMR}$ (DMSO-d_6): δ 3.73 (s, 3H, OCH_3), 4.23 (d, $^4J_{\text{H-H}} = 1.6$ Hz, 2H, $\text{H}_2\text{C-N}_3$), 6.28 [t, $^4J_{\text{H-H}} = 1.6$ Hz, 1H, $=\text{CHC}(\text{O})$], 7.34 (t, $J_{\text{H-H}} = 7.4$ Hz, 2H, 6'-H and 7'-H), 7.56 (d, $J_{\text{H-H}} = 7.8$ Hz, 2H, 5'-H and 8'-H), 8.45 ppm (s, 1H, 4'-H); $^{13}\text{C-NMR}$ (DMSO-d_6): δ 162.5, 161.8 (2C=O), 153.7 (9'-C), 146.7 (3'-C–C=), 141.7 (4'-C), 133.3, 126.4, 125.6, 118.7, 114.2 (7'-C, 8'-C, 5'-C, 6'-C, 10'-C), 113.2 (3'-C), 112.8 [$=\text{CHC}(\text{O})$], 56.5 ($\text{H}_2\text{C-N}_3$), 52.6 ppm (OCH_3 , ester); ms: m/z (EI): 286 (9) [$\text{M}^+ + 1$], 285 (17) [M^+], 254 (11), 243 (100), 225 (32), 198 (28), 171 (43), 170 (19), 142 (10), 114 (8). Anal. Calcd for $\text{C}_{14}\text{H}_{11}\text{N}_3\text{O}_4$ (285.3): C, 58.95; H, 3.89; N, 14.73. Found: C, 59.01; H, 3.84; N, 14.67.

Ethyl (2Z)-4-azido-3-(2-oxo-2H-chromen-3-yl)but-2-enoate (11b). This was obtained as yellow leaflets, 710 mg (68%); mp 128–130°C (cyclohexane); IR: ν_{max} N₃ 2102, C=O (lactone) 1720, C=O (ester) 1714, C=C (exocyclic) 1608 cm^{-1} ; $^1\text{H-NMR}$ (DMSO-d_6): δ 1.23 (t, 3H, $J_{\text{H-H}} = 6.8$ Hz, OC-CH_3), 4.08 (q, $J_{\text{H-H}} = 6.8$ Hz, 2H, OCH_2 , ester), 4.39 [d, 2H, $^4J_{\text{H-H}} = 1.8$ Hz, $\text{H}_2\text{C-N}_3$], 6.08 [t, $^4J_{\text{H-H}} = 1.8$ Hz, 1H, $=\text{CHC}(\text{O})$], 7.34 (t, $J_{\text{H-H}} = 7.4$ Hz, 2H, 6'-H and 7'-H), 7.56 (d, $J_{\text{H-H}} = 7.8$ Hz, 2H, 5'-H and 8'-H), 8.42 ppm (s, 1H, 4'-H); $^{13}\text{C-NMR}$ (DMSO-d_6): δ 163.2, 162.6 (2C=O), 152.8 (9'-C), 145.6 (3'-C–C=), 140.1 (4'-C), 132.7, 127.1, 125.8, 118.8, 114.2 (7'-C, 8'-C, 5'-C, 6'-C, 10'-C), 113.7 (3'-C), 112.6 [$=\text{CHC}(\text{O})$], 62.6 (OCH_2 , 56.5 ($\text{H}_2\text{C-N}_3$), 15.6 ppm (OC-CH_3); ms: m/z (EI): 300 (11) [$\text{M}^+ + 1$], 299 (22) [M^+], 257 (100), 242 (18), 225 (35), 198 (25), 171 (16), 142 (10), 114 (8); Anal. Calcd for $\text{C}_{15}\text{H}_{13}\text{N}_3\text{O}_4$ (299.2): C, 60.20; H, 4.38; N, 14.04. Found: C, 60.27; H, 4.43; N, 14.13.

(2Z)-4-Azido-3-(2-oxo-2H-chromen-3-yl)but-2-enitrile (11c). This was obtained as yellow leaflets, 669 mg (76%); mp 148–150°C (EtOH); IR: ν_{max} CN 2216, N₃ 2102, C=O (lactone) 1721, C=C (exocyclic) 1607 cm^{-1} ; $^1\text{H-NMR}$ (DMSO-d_6): δ 4.44 (d, $^4J_{\text{H-H}} = 2.1$ Hz, 2H, $\text{H}_2\text{C-N}_3$), 6.26 (t, $^4J_{\text{H-H}} = 2.1$ Hz, 1H, $=\text{CHCN}$), 7.33 (t, $J_{\text{H-H}} = 7.4$ Hz, 2H, 6'-H and 7'-H), 7.55 (d, $J_{\text{H-H}} = 7.8$ Hz, 2H, 5'-H and 8'-H), 8.45 ppm (s, 1H, 4'-H); $^{13}\text{C-NMR}$ (DMSO-d_6): δ 161.2 (C=O), 154.7 (9'-C), 148.6 (C=C–CN), 139.7 (4'-C), 132.3, 130.5, 126.4, 118.7, 114.2 (7'-C, 8'-C, 5'-C, 6'-C, 10'-C), 120.4 (3'-C), 115.6 (CN), 98.6 ($=\text{CHCN}$), 52.3 ppm ($\text{H}_2\text{C-N}_3$); ms: m/z (EI): 253 (11) [$\text{M}^+ + 1$], 252 (16) [M^+], 224 (77), 210 (48), 197 (100), 169 (85), 140 (42), 114 (13); Anal. Calcd for $\text{C}_{13}\text{H}_8\text{N}_4\text{O}_2$ (252.2): C, 61.90; H, 3.20; N, 22.21. Found: C, 61.96; H, 3.24; N, 22.16.

Reaction of 1 with phosphonium salts 13a,b. **Preparation of 14a and 15.** A dimethylformamide (DMF) solution of 3.5 mmol methyltriphenylphosphonium bromide **13a** (or benzyltriphenylphosphonium chloride, **13b**) and the azide **1** (0.8 g, 3.5 mmol) was treated with aqueous LiOH. The reaction mixture was stirred at r.t. for 24 h. The product mixture was concen-

trated to 10 mL, diluted with 30 mL of dist H_2O , acidified with conc. HCl, and then extracted with two portions of ethyl acetate. The AcOEt extracts were combined and washed with 50 mL of dist H_2O and dried, and the solvents were evaporated to dryness. The residue was purified by column chromatography with *n*-hexane /AcOEt as the eluents, whereupon compounds **14a** and **15**, were obtained. Ph_3PO was also isolated.

3-[1-(Azidomethyl)vinyl]-2H-chromen-2-one (14a). This was obtained as yellow leaflets, 635 mg (80%); mp 173–175°C (acetone); IR: ν_{max} C–N₃ 2106, C=O (lactone) 1720, C=C (exocyclic) 1618 cm^{-1} ; $^1\text{H-NMR}$ (DMSO-d_6): δ 4.02 (t, $J_{\text{H-H}} = 2.2$ Hz, 2H, H_2CN_3), 5.45, 5.66 (2t(br), $2 \times 1\text{H}$, $=\text{CH}_2$), 7.28 (t, $J_{\text{H-H}} = 7.4$ Hz, 2H, 6'-H and 7'-H), 7.54 (d, $J_{\text{H-H}} = 7.8$ Hz, 2H, 5'-H and 8'-H), 8.43 ppm (s, 1H, 4'-H); $^{13}\text{C-NMR}$ (DMSO-d_6): δ 156.2 (2'-C=O), 154.2 (9'-C), 139.7 (C=CH₂), 132.3, 129.5, 128.4, 126.4, 118.7, 117.2 (7'-C, 4'-C, 5'-C, 6'-C, 8'-C, 10'-C), 120.4 (3'-C), 114.2 (C=CH₂), 60.2 ppm ($\text{H}_2\text{C-N}_3$); ms: m/z (EI): 228 (11) [$\text{M}^+ + 1$], 227 (16) [M^+], 185 (44), 167 (48), 149 (100), 99 (65), 77 (28); Anal. Calcd for $\text{C}_{12}\text{H}_9\text{N}_3\text{O}_2$ (227.2): C, 63.43; H, 3.99; N, 18.49. Found: C, 63.51; H, 3.96; N, 18.43.

3-[(E,Z)-2-Azido-1-benzylvinyl]-2H-chromen-2-one (15). This was obtained as yellow leaflets, 890 mg (84%); mp 198–200°C (CHCl_3 , mixture of isomers *E* and *Z*, 50:50); IR: ν_{max} C–N₃ 2108, C=O (lactone) 1721, C=C (exocyclic) 1617 cm^{-1} ; $^1\text{H-NMR}$ (DMSO-d_6): *E* isomer: δ 3.38 (d, 2H, $J_{\text{H-H}} = 2.1$ Hz, CH_2), 7.18 (t, $J_{\text{H-H}} = 2.1$ Hz, 1H, $=\text{CHN}_3$), 7.24–7.38 (m, 3H, *H*-Ph and *H*-Ar, *E*, *Z*), 7.45–7.67 (m, 6H, *H*-Ph and *H*-Ar, *E*, *Z*), 8.46, 8.54 ppm (2s, $2 \times 1\text{H}$, 4'-H, *E*, *Z*); *Z* isomer: δ 3.47 (d, 2H, $J_{\text{H-H}} = 2.2$ Hz, CH_2), 7.23 (t, $J_{\text{H-H}} = 2.2$ Hz, 1H, $=\text{CHN}_3$); ms: m/z (EI): 304 (13) [$\text{M}^+ + 1$], 303 (21) [M^+], 275 (100), 256 (77), 210 (21), 149 (44), 137 (36), 111 (13), 77 (58); Anal. Calcd for $\text{C}_{18}\text{H}_{13}\text{N}_3\text{O}_2$ (303.3): C, 71.28; H, 4.32; N, 13.85. Found: C, 71.33; H, 4.37; N, 13.90.

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